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Laser Temperature Jump Studies

The primary objective of research under this grant has been the development of a laser temperature jump apparatus capable of measuring submicrosecond relaxations of light absorbance associated with very rapid chemical reactions occurring in liquid solutions. During the grant year, we published a paper¹ reporting the successful measurement of relaxations with durations of several tens of microseconds occurring in aqueous azo dye solutions. A Q-switched neodymium doped glass laser with a ~ 1 joule output rapidly heated submilliliter volumes of aqueous solution to achieve these results. A less intense, continuous monochromatic light beam at right angles to the laser beam that passed through the heated volume of solutions and was directed onto the photocathode of a photomultiplier tube was used to detect the chemical effects of the rapid $\sim 5^\circ$ rise in temperature of the sample solution.

At Case-Western Reserve a similar research program resulted in the development of a laser temperature jump apparatus that used conductimetric rather than spectrophotometric detection of the chemical relaxation times.² The conductimetric technique has the advantage of greater sensitivity to small, rapid concentration changes but the disadvantage of a more restricted range of suitable sample equilibria: those involving charge neutralization or at least a dramatic change in conductivity upon displacement of the chemical equilibrium. Hoffmann *et al.*² were unable to measure relaxation times under about 3 μ sec but did report chemical relaxations as short as 25 μ sec in 0.2 M aqueous nickel acetate at several temperatures.

It would have been interesting to extend our spectrophotometric laser temperature jump technique to the submicrosecond time range by using a Q-switch neodymium

(1) W. H. Inskeep, D. L. Jones, W. T. Silfvast, and E. M. Eyring, *Proc Natl. Acad. Sci. U.S.*, 59, 1027 (1968).

(2) H. Hoffmann, E. Yeager, and J. Stuehr, *Rev. Sci. Instrum.*, 39, 649 (1968).

laser with a larger output energy per pulse. Since funds were not available to purchase a tandem oscillator-amplifier laser system³, we elected instead to explore two longer time scale applications of our then available laser temperature jump equipment: the measurement of a relaxation time associated with a suspected reaction of cupric ion in a fused alkali nitrate salt-solvent and the measurement of the rate of the reaction of ferric ion with thiocyanate ion in water over a very wide temperature range.

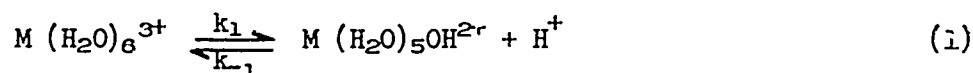
In the case of the cupric ion-fused salt system, there is a large change in the 355 mμ extinction coefficient with temperature in an extended range around 300° C. We believe that the cooling down of the melt by thermal diffusion following the laser pulse was responsible for the ~ 150 millisecond observed relaxation times. Had we had enough energy in the laser pulse to heat a larger sample volume, it might have been possible to measure the rate of nitrate ion exchange in the first coordination sphere of cupric ion in this type of high temperature solvent.

The aqueous $\text{Fe}^{3+} + \text{SCN}^-$ sample system was more tractable, and we did observe millisecond relaxation times consistent with the known rate constants for this well studied system.⁴ However, the precision of our sample thermostating was insufficient to permit the determination of improved values of the previously reported activation parameters.

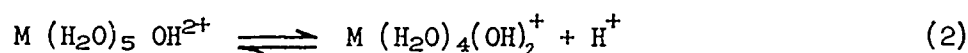
E-Jump Metal Ion Hydrolysis Studies

Utilizing an electric field jump (E-jump) relaxation method apparatus previously described,^{5,6} we measured the specific rate of the reaction

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- (3) A. F. Haught, *Ann. Rev. Phys. Chem.*, 19, 343 (1968).
 - (4) For references see E. F. Caldin, Fast Reactions in Solution, John Wiley and Sons, New York, 1964, p. 49.
 - (5) D. T. Rampton, L. P. Holmes, D. L. Cole, R. P. Jensen, and E. M. Eyring, *Rev. Sci. Instrum.*, 38, 1637 (1967).
 - (6) D. L. Cole, E. M. Eyring, D. T. Rampton, A. Silzars, and R. P. Jensen, *J. Phys. Chem.*, 71, 2771 (1967).



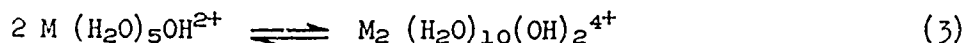
for the aqueous metal ion perchlorate systems shown in Table I. A representative plot of experimental data for gallium (III) and chromium (III) are shown in Figure 1. Although the equilibrium



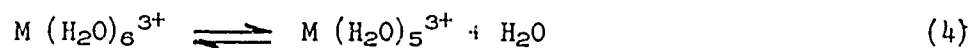
is also almost certainly present to a significant extent in every system except that of aluminum (III), we detected only a single microsecond-time-range relaxation in each of these systems. Our experimental results for the chromium (III)⁷ and scandium (III) perchlorates⁸ suggest that reactions 1 and 2 are coupled in such a way that the amplitude of the conductance change associated with the second reaction is indetectably small compared to that of reaction 1.

Our kinetic results regarding reaction 1 (Table I) can be summarized thusly:

There is no kinetic evidence for more than one monomeric hydrolysis step in freshly prepared, dilute, aqueous solutions of these trivalent metal ions. On the other hand, our Joule heating temperature jump relaxation times in the millisecond time range for aqueous Sc^{3+} , In^{3+} , and Ga^{3+} convincingly confirm the presence of previously reported⁹ dimerizations of the type



Quite unlike the specific rate of inner coordination sphere water loss

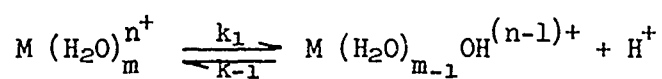


(7) L. D. Rich, D. L. Cole, and E. M. Eyring, J. Phys. Chem., in press.

(8) D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, Inorg. Chem., in press.

(9) For references see L. G. Sillen, Stability Constants of Metal-Ion Complexes, Section I: Inorganic Ligands, The Chemical Society, London, 1964.

Table I: Aqueous metal ion hydrolyses



in aqueous solutions of ionic strength $\mu < 10^{-3}$ M at 25°.

$M(H_2O)_m^{n+}$	Ionic radius, Å	k_{-1} , $10^9 \text{ M}^{-1}\text{sec}^{-1}$	k_1 , 10^5 sec^{-1}
UO_2^{2+}		16.5	0.17
Al^{3+}	0.57	4.4	1.1
Cr^{3+}	0.65	0.78	1.4
Ga^{3+}	0.62	4.4	2.7
In^{3+}	0.81	9.1	1.1
Sc^{3+}	0.83	10	1.7
Er^{3+}	1.04	32	2.8
Th^{4+}	1.10	0.7	0.9

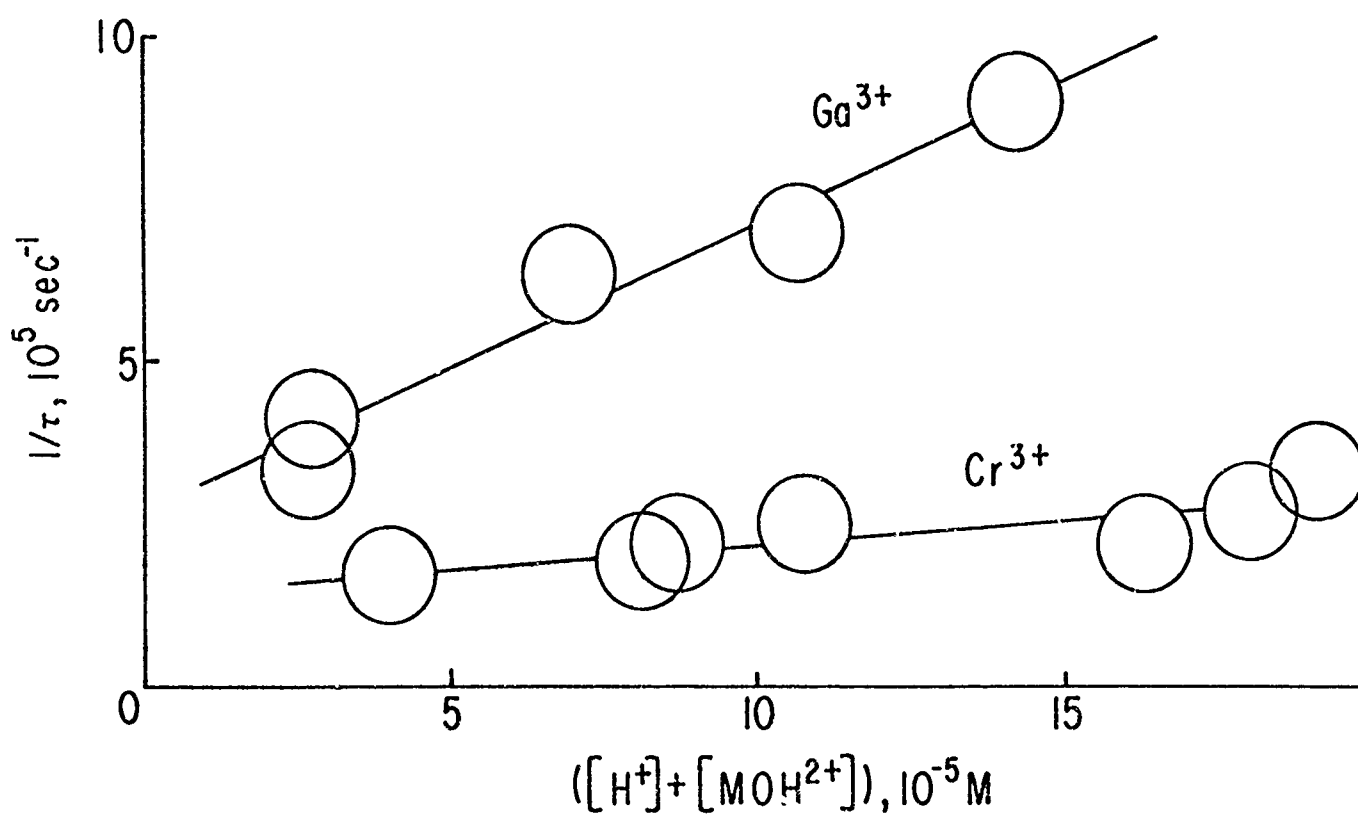


Figure 1. Representative electric field jump data points for the hydrolysis of aqueous gallium (III) and chromium (III) perchlorate at 25°. The reciprocal of the experimental relaxation time τ is plotted as ordinate and a sum of concentrations as abscissa.

that ranges over many powers of ten for these same ions,^{10,11} k_1 of reaction 1 is essentially independent of the radii of the metal ions.

Finally, the specific rate of ion recombination, k_{-1} in reaction 1, is essentially diffusion controlled and roughly proportional to metal ion radii except for chromium (III).

These results can be used to estimate rate constants k_1 and k_{-1} for reaction 1 involving metal ions that are presently inaccessible to our relaxation techniques such as Ce^{4+} , Hg^{2+} , Be^{2+} , Zn^{2+} , and titanium (IV).

The principal items of unfinished business are the preparation for publication of our results on gallium (III), indium (III) and erbium (III); the completion of a similar study of iron (III); and the development of a more complete explanation for our inability to observe a second microsecond E-jump relaxation in these hydrolysis systems.

During the same fifteen month research grant period reported here we also prepared and published a review article¹² that acknowledges AFOSR support.

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- (10) M. Eigen and R. G. Wilkins, in Mechanisms of Inorganic Reactions, Advances in Chemistry Series No. 49, R. K. Murmann, R. T. M. Fraser, and J. Bauman, Eds., American Chemical Society, Washington, D. C., 1965, pp. 55-67.
- (11) D. Fiat and R. E. Connick, J. Am. Chem. Soc., 90, 608 (1968).
- (12) E. M. Eyring and B. C. Bennion, Ann. Rev. Phys. Chem., 19, 129 (1968).

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2. J. L. Haslam, E. M. Eyring, W. W. Epstein, R. P. Jensen, and C. W. Jaeger, "Equilibrium and Kinetic Studies of the Deprotonation of the Monoanion of Several Dicarboxylic Acids in Water and in Deuterium Oxide," J. Am. Chem. Soc., 87, 4247 (1965).
3. E. M. Eyring and J. L. Haslam, "Solvent Deuterium Isotope Effects on Intramolecularly Hydrogen-Bonded Dicarboxylic Acid Monoanions," J. Phys. Chem., 70, 293 (1966).
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5. W. H. Inskip, D. L. Jones, W. T. Silfvast, and E. M. Eyring, "Intramolecular Hydrogen Bonding of Azo Dyes in Aqueous Solution," Proc. Natl. Acad. Sci. U. S., 59, 1027 (1968).
6. E. M. Eyring and B. C. Bennion, "Fast Reactions in Solution," Ann. Rev. Phys. Chem., 19, 129 (1968).
7. D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, "Kinetics of Aqueous Scandium (III) Perchlorate Hydrolysis and Dimerization," Inorg. Chem., in press.
8. L. D. Rich, D. L. Cole, and E. M. Eyring, "Hydrolysis Kinetics of Dilute Aqueous Chromium (III) Perchlorate," J. Phys. Chem., in press.
9. L. D. Rich, D. L. Cole, and E. M. Eyring, "Hydrolysis Kinetics of Dilute Aqueous Gallium (III), Indium (III), and Erbium (III) Perchlorates," in preparation.
10. D. L. Cole, L. D. Rich, and E. M. Eyring, "Kinetics of Hydrolysis of Aqueous Ferric Ion," in preparation.

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13. ABSTRACT Progress is reported on two major lines of investigation: Microsecond-time-range measurements of rates of protolytic reactions of aqueous azo dyes have been published that were obtained in part with a laser temperature jump apparatus. Publication by another research group of similar laser temperature jump data is noted. Laser temperature jump studies of cupric ion in a fused alkali nitrate salt solvent and of the reaction in aqueous solution between ferric ion and thiocyanate ion were unsuccessful primarily because the laser pulses were not sufficiently energetic. A concurrent electric field jump relaxation method rate study of metal ion hydrolyses is also reported. Investigation of aqueous chromium (III), scandium (III), gallium (III), and indium (III) perchlorates led to generalizations regarding the forward and backward reaction rate constants. Confirmation of the existence of rapid polymerization equilibria in these systems was also provided.		

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	Ferric ion						
	Thiocyanate ion						
	Hydrolysis rates						
	Scandium (III) perchlorate						
	Indium (III) perchlorate						
	Gallium (III) perchlorate						
	Chromium (III) perchlorate						
	Rapid polymerizations						

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